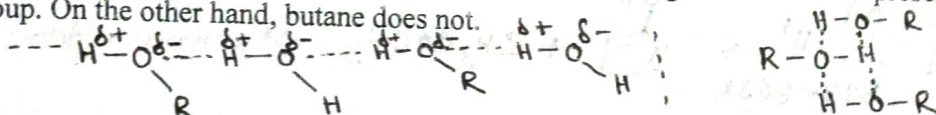


## Alcohols phenols and ethers

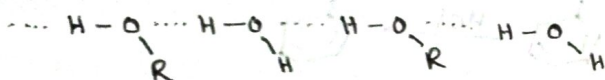
Question 1: Explain why propanol has higher boiling point than that of the hydrocarbon, butane?

Solution 1: Propanol undergoes intermolecular H-bonding because of the presence of —OH group. On the other hand, butane does not.



Therefore, extra energy is required to break hydrogen bonds. For this reason, propanol has a higher boiling point than hydrocarbon butane.

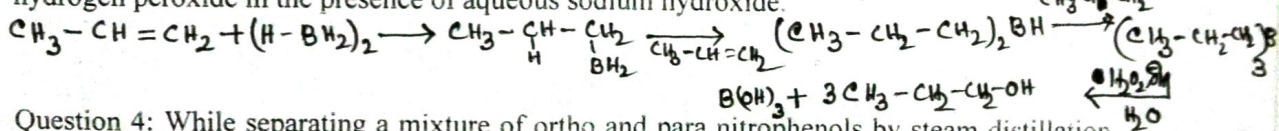
Question 2: Alcohols are comparatively more soluble in water than hydrocarbons of comparable molecular masses. Explain this fact.



Solution 2: Alcohols form H-bonds with water due to the presence of -OH group. However, hydrocarbons cannot form H-bonds with water. As a result, alcohols are comparatively more soluble in water than hydrocarbons of comparable molecular masses.

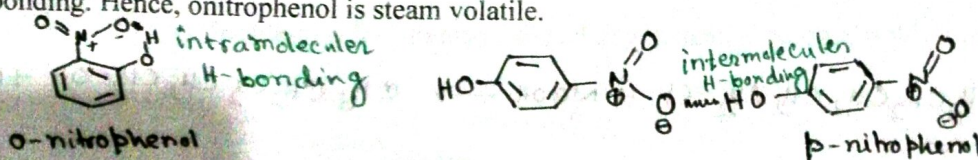
Question 3: What is meant by hydroboration-oxidation reaction? Illustrate it with an example.

Solution 3: The addition of borane followed by oxidation is known as the hydroboration-oxidation reaction. For example, propan-1-ol is produced by the hydroboration-oxidation reaction of propene. In this reaction, propene reacts with diborane (B<sub>2</sub>H<sub>6</sub>) (BH<sub>3</sub> to form trialkylborane as an addition product. This addition product is oxidized to alcohol by hydrogen peroxide in the presence of aqueous sodium hydroxide.



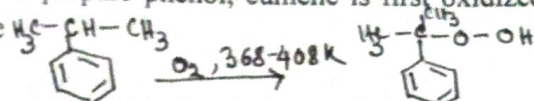
Question 4: While separating a mixture of ortho and para nitrophenols by steam distillation, name the isomer which will be steam volatile. Give reason.

Solution 4: Intramolecular H-bonding is present in o-nitrophenol and p-nitrophenol. In p-nitrophenol, the molecules are strongly associated due to the presence of intermolecular bonding. Hence, onitrophenol is steam volatile.

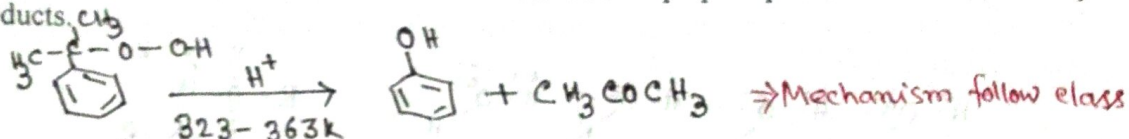


Question 5: Give the equations of reactions for the preparation of phenol from cumene

Solution 5: To prepare phenol, cumene is first oxidized in the presence of air of cumene hydroperoxide

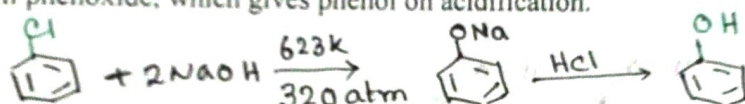


Then, cumene hydroperoxide is treated with dilute acid to prepare phenol and acetone as by products



Question 6: Write chemical reaction for the preparation of phenol from chlorobenzene.

Solution 6: Chlorobenzene is fused with NaOH (at 623 K and 320 atm pressure) to produce sodium phenoxide, which gives phenol on acidification.

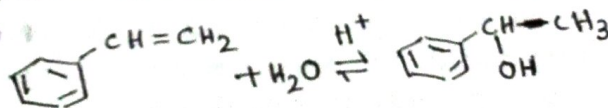


Question 7: Show how will you synthesize: (I) 1-phenylethanol from a suitable alkene.

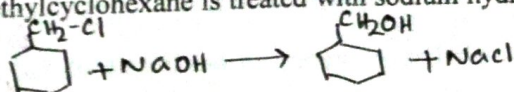
(ii) cyclohexylmethanol using an alkyl halide by an SN2 reaction.

(iii) pentan-1-ol using a suitable alkyl halide?

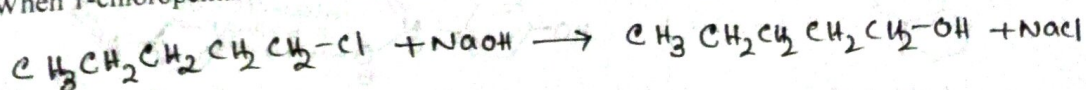
Solution 7: (i) By acid-catalysed hydration of ethylbenzene (styrene), 1-phenylethanol can be synthesized



(ii) When chloromethylcyclohexane is treated with sodium hydroxide, cyclohexylmethanol is obtained.

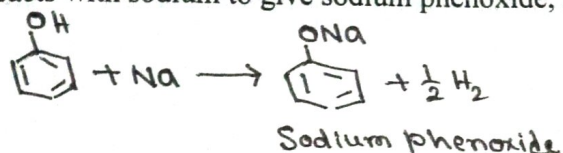


(iii) When 1-chloropentane is treated with NaOH, pentan-1-ol is produced.

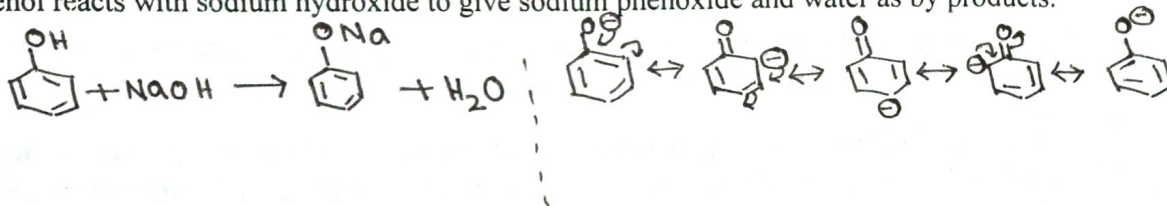


Question 8: Give two reactions that show the acidic nature of phenol. Compare acidity of phenol with that of ethanol.

Solution 8: The acidic nature of phenol can be represented by the following two reactions: (i) Phenol reacts with sodium to give sodium phenoxide, liberating  $H_2$ .



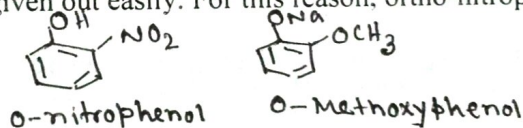
(ii) Phenol reacts with sodium hydroxide to give sodium phenoxide and water as by products.



The acidity of phenol is more than that of ethanol. This is because after losing a proton, the phenoxide ion undergoes resonance and gets stabilized whereas ethoxide ion does not.

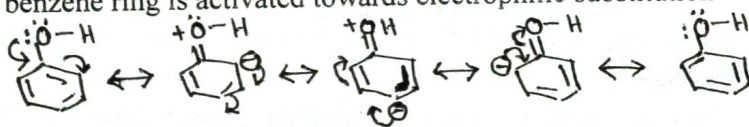
Question 9: Explain why is ortho nitrophenol more acidic than ortho methoxyphenol?

Solution 9: The nitro-group is an electron-withdrawing group. The presence of this group in the ortho position decreases the electron density in the O-H bond. As a result, it is easier to lose a proton. Also, the o-nitrophenoxide ion formed after the loss of protons is stabilized by resonance. Hence, ortho-nitrophenol is a stronger acid. On the other hand, methoxy group is an electron-releasing group. Thus, it increases the electron density in the O-H bond and hence, the proton cannot be given out easily. For this reason, ortho-nitrophenol is more acidic than ortho-methoxyphenol.



Question 10: Explain how does the -OH group attached to a carbon of benzene ring activate it towards electrophilic substitution?

Solution 10: The -OH group is an electron-donating group. Thus, it increases the electron density in the benzene ring as shown in the given resonance structure of phenol. As a result, the benzene ring is activated towards electrophilic substitution.



11. Monochlorination of toluene in sunlight followed by hydrolysis with aq. NaOH yields.

(i) o-Cresol (ii) m-Cresol (iii) 2, 4-Dihydroxytoluene (iv) Benzyl alcohol (Ans. (iv) Benzyl alcohol)

Explanation: Monochlorination of toluene in sunlight gives benzyl chloride. On hydrolysis with aq. NaOH, benzyl chloride, shows nucleophilic substitution reaction to give benzyl alcohol.

12.  $\text{CH}_3\text{CH}_2\text{OH}$  can be converted into  $\text{CH}_3\text{CHO}$  by \_\_\_\_\_.

(i) catalytic hydrogenation (ii) treatment with  $\text{LiAlH}_4$  (iii) treatment with pyridinium chlorochromate (iv) treatment with  $\text{KMnO}_4$

Ans. (iii) treatment with pyridinium chlorochromate Explanation: A better reagent for oxidation of primary alcohols to aldehydes in good yield is pyridinium chlorochromate (PCC), a complex of chromium trioxide with pyridine and HCl.

13. The process of converting alkyl halides into alcohols involves \_\_\_\_\_.

(i) addition reaction (ii) substitution reaction (iii) dehydrohalogenation reaction (iv) rearrangement reaction

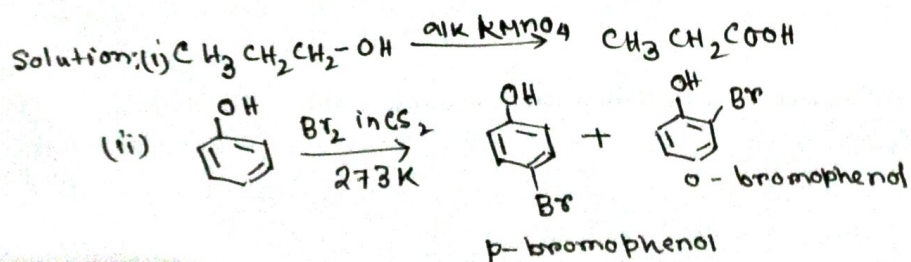
Ans. (ii) substitution reaction Explanation: The reaction is a type of nucleophilic substitution reaction in which  $-\text{Cl}$  group is replaced by  $-\text{OH}$ .

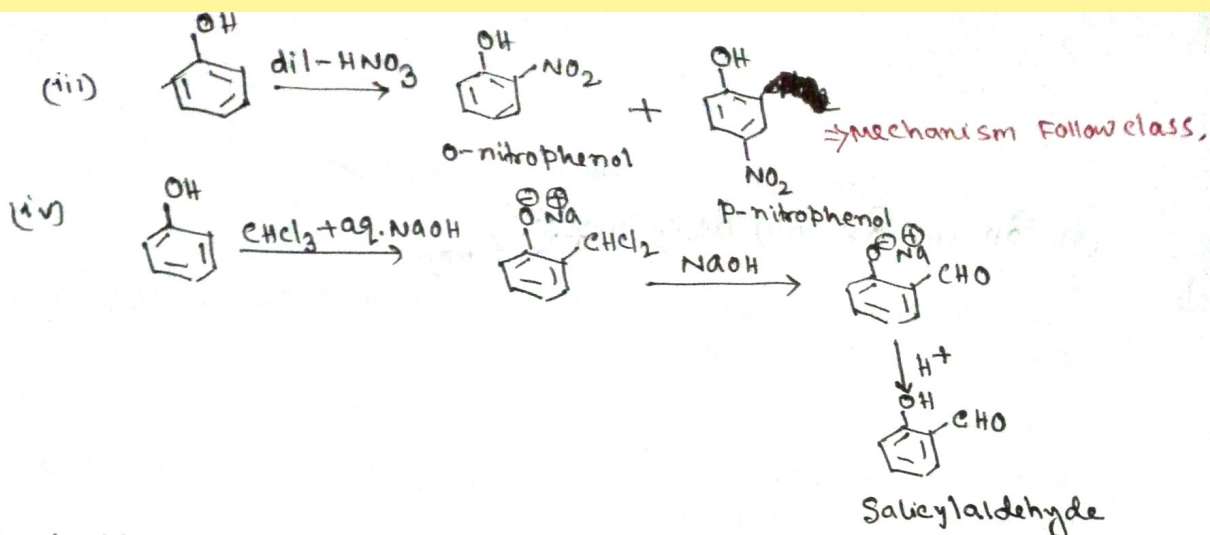
14. IUPAC name of m-cresol is \_\_\_\_\_.

(i) 3-methylphenol (ii) 3-chlorophenol (iii) 3-methoxyphenol (iv) benzene-1,3-diol (Ans. (i) 3-methylphenol)

Question 15: Give equations of the following reactions:

- (i) Oxidation of propan-1-ol with alkaline  $\text{KMnO}_4$  solution.  
 (ii) Bromine in  $\text{CS}_2$  with phenol  
 (iii) Dilute  $\text{HNO}_3$  with phenol.  
 (iv) Treating phenol with chloroform in presence of aqueous NaOH.

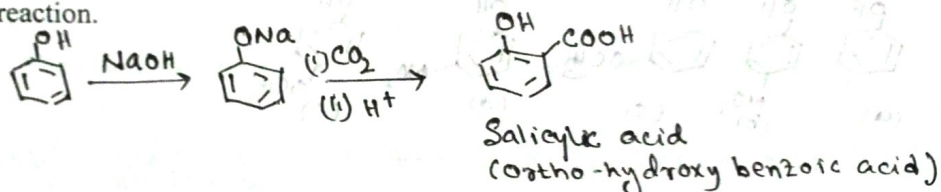




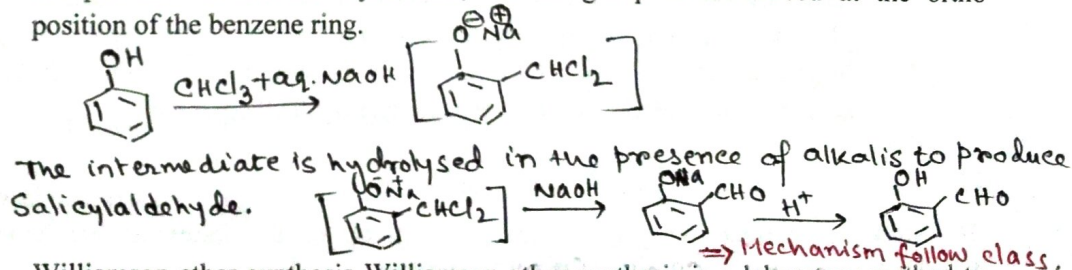
Question 16: Explain the following with an example.

- (i) Kolbe's reaction. (ii) Reimer-Tiemann reaction. (iii) Williamson ether synthesis. (iv) Unsymmetrical ether

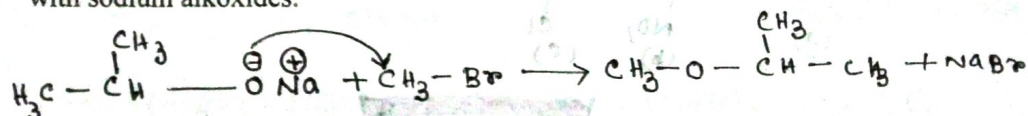
- (ii) Solution 18: (i) Kolbe's reaction: When phenol is treated with sodium hydroxide, sodium phenoxide is produced. This sodium phenoxide when treated with carbon dioxide, followed by acidification, undergoes electrophilic substitution to give ortho-hydroxybenzoic acid as the main product. This reaction is known as Kolbe's reaction.



- (iii) Reimer-Tiemann reaction: When phenol is treated with chloroform ( $\text{CHCl}_3$ ) in the presence of sodium hydroxide, a-CHO group is introduced at the ortho position of the benzene ring.

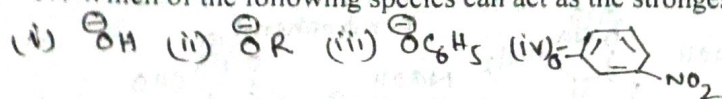


- (iv) Williamson ether synthesis Williamson ether synthesis is a laboratory method to prepare symmetrical and unsymmetrical ethers by allowing alkyl halides to react with sodium alkoxides.



If the alkyl halide is secondary or tertiary, then elimination competes over substitution.

17. Which of the following species can act as the strongest base?



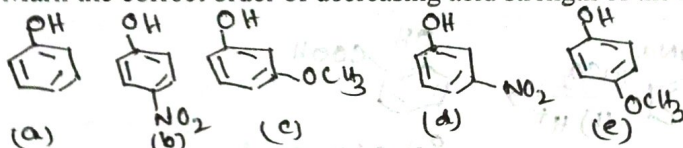
Ans. (ii) Explanation: Weakest acid has the strongest conjugate base. Among all the four options ROH is the weakest acid.

18. Phenol is less acidic than \_\_\_\_\_. (i) ethanol (ii) o-nitrophenol (iii) o-methylphenol (iv) o-methoxyphenol

Ans. (ii) o-nitrophenol

Explanation: In substituted phenols, the presence of electron withdrawing group such as nitro group, enhances the acidic strength of phenol. This effect is more pronounced when such a group is present at ortho and para positions. It is due to the effective delocalisation of negative charge in phenoxide ion. On the other hand, electron releasing groups, such as alkyl groups, in general, do not favour the formation of phenoxide ion resulting in decrease in acid strength. Cresols, for example, are less acidic than phenol.

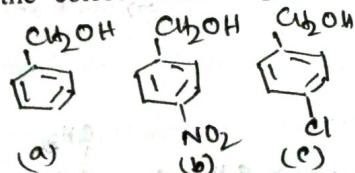
19. Mark the correct order of decreasing acid strength of the following compounds.



(i) e > d > b > a > c (ii) b > d > a > c > e (iii) d > e > c > b > a (iv) e > d > c > b > a

(ii) Ans. (ii) b > d > a > c > e Explanation: In substituted phenols, the presence of electron withdrawing group such as nitro group, enhances the acidic strength of phenol. This effect is more pronounced when such a group is present at ortho and para positions. It is due to the effective delocalisation of negative charge in phenoxide ion. On the other hand, electron releasing groups, such as alkyl groups, in general, do not favour the formation of phenoxide ion resulting in decrease in acid strength. Cresols, for example, are less acidic than phenol.

20. Mark the correct increasing order of reactivity of the following compounds with HBr/HCl.



⇒ Follow class

(i) a < b < c (ii) b < a < c ~~\_\_\_\_\_~~ (iii) b < c < a (iv) c < b < a

(ii) Ans. (iii) b < c < a

Explanation: It is type of nucleophilic substitution reaction followed by SN1 mechanism. SN1 mechanism depends on the stability of carbocation. Presence of electron withdrawing group will decrease the stability of carbocation.

21. Arrange the following compounds in increasing order of boiling point. Propan-1-ol, butan-1-ol, butan-2-ol, pentan-1-ol

(i) Propan-1-ol, butan-2-ol, butan-1-ol, pentan-1-ol (ii) Propan-1-ol, butan-1-ol, butan-2-ol, pentan-1-ol (iii) Pentan-1-ol, butan-2-ol, butan-1-ol, propan-1-ol (iv) Pentan-1-ol, butan-1-ol, butan-2-ol, propan-1-ol

Ans. (i) Propan-1-ol, butan-2-ol, butan-1-ol, pentan-1-ol

Explanation: The boiling points of alcohols and phenols increase with increase in the number of carbon atoms (increase in van der Waals forces.). In alcohols, the boiling points decrease with increase of branching in carbon chain (because of decrease in van der Waals forces with decrease in surface area.)

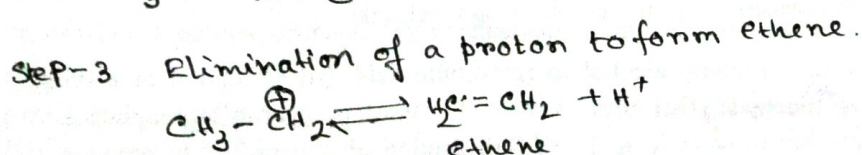
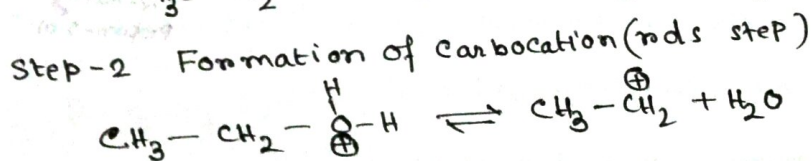
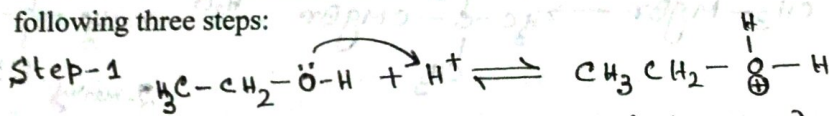
22. Phenol can be distinguished from ethanol by the reactions with \_\_\_\_\_. (i) Br<sub>2</sub> /water (ii) Na (iii) Neutral FeCl<sub>3</sub> (iv) All the above

Ans. (i) and (iii)

Explanation: Ethanol does not give any reaction with neutral FeCl<sub>3</sub> solution while phenol gives violet color with neutral FeCl<sub>3</sub>. When phenol is treated with bromine water, 2,4,6-tribromophenol is formed as white precipitate. Ethanol does not react with bromine water.

Question 23: Write the mechanism of acid-catalyzed dehydration of ethanol to yield ethene.

Solution 23: The mechanism of acid dehydration of ethanol to yield ethene involves the following three steps:

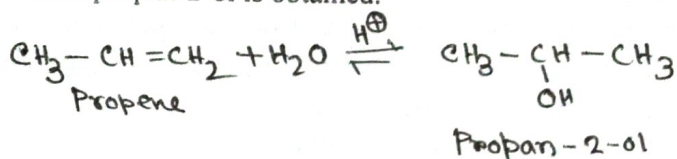


Question 24: How are the following conversions carried Out? (i) Propene → Propan-2-ol

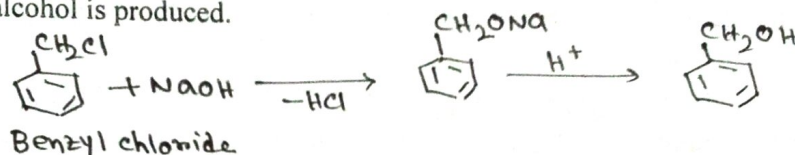
- (ii) Benzyl chloride.  $\rightarrow$  Benzyl alcohol (iii) Ethyl magnesium chloride  $\rightarrow$  Propan-1-ol. (iv) Methyl magnesium bromide  $\rightarrow$  2-Methylpropan-2-ol.

Solution 24:

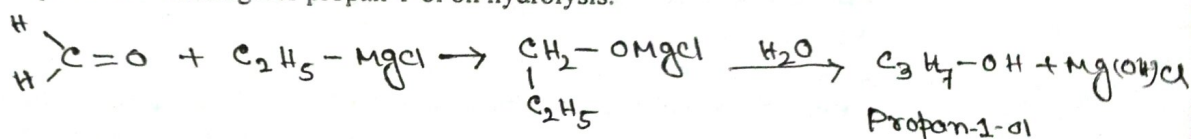
- (i) If propene is allowed to react with water in the presence of an acid as a catalyst, then propan-2-ol is obtained.



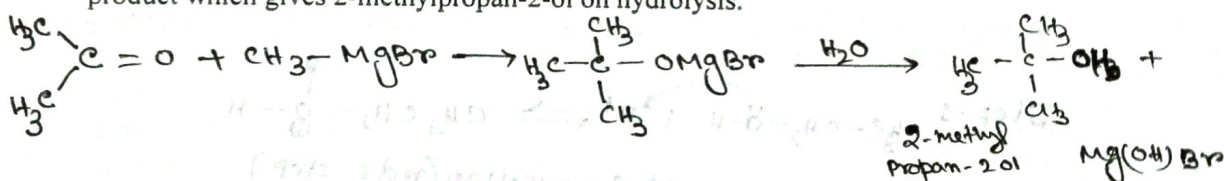
- (ii) If benzyl chloride is treated with NaOH (followed by acidification) then benzyl alcohol is produced.



- (iii) When ethyl magnesium chloride is treated with methanal, an adduct is the produced which gives propan-1-ol on hydrolysis.



- (iv) When methyl magnesium bromide is treated with propanone, an adduct is the product which gives 2-methylpropan-2-ol on hydrolysis.



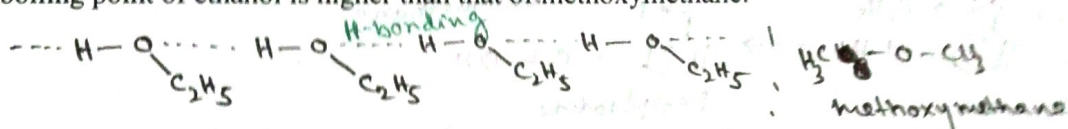
Question 25: Name the reagents used in the following reactions:

- (i) Oxidation of a primary alcohol to carboxylic acid. (ii) Oxidation of a primary alcohol to aldehyde. (iii) Bromination of phenol to 2,4,6-tribromophenol. (iv) Benzyl alcohol to benzoic acid. (v) Dehydration of propan-2-ol to propene. (vi) Butan-2-one to butan-2-ol.
- (ii) Solution 21: (i) Acidified potassium permanganate (ii) Pyridinium chlorochromate (PCC) (iii) Bromine water (iv) Acidified potassium permanganate (v) 85% phosphoric acid at 440 K (vi) NaBH or LiAlH<sub>4</sub>

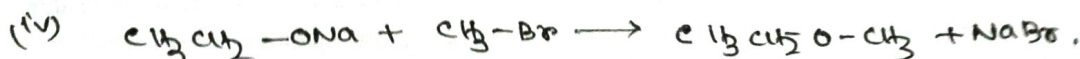
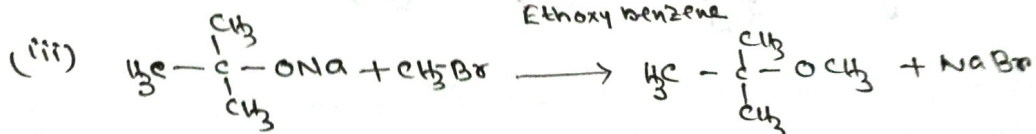
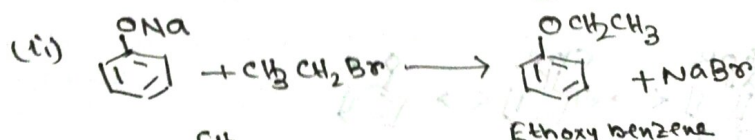
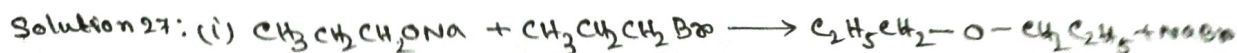


Question 26: Give reason for the higher boiling point of ethanol in comparison to methoxymethane.

Solution 26: Ethanol undergoes intermolecular H-bonding due to the presence of  $-\text{OH}$  group, resulting in the association of molecules. Extra energy is required to break these hydrogen bonds. On the other hand, methoxymethane does not undergo H-bonding. Hence, the boiling point of ethanol is higher than that of methoxymethane.

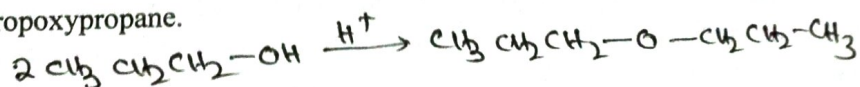


Question 27: Write the names of reagents and equations for the preparation of the following ethers by Williamson's synthesis: (i) 1-Propoxypropane (ii) Ethoxybenzene (iii) 2-Methoxy-2-methylpropane (iv) 1-Methoxyethane

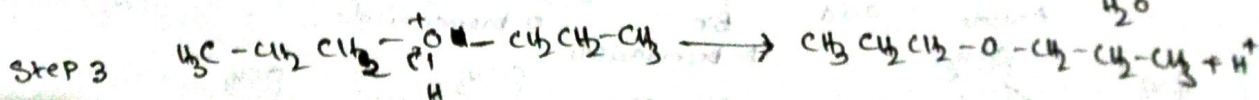
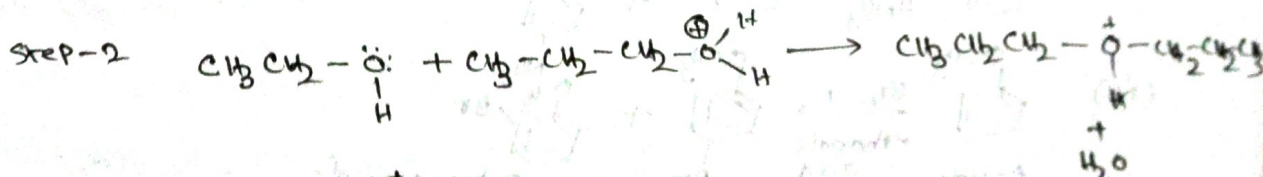
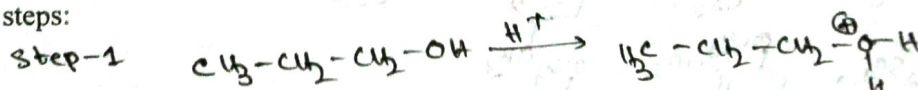


Question 28: How is 1-propoxypropane synthesised from propan-1-ol? Write mechanism of this reaction.

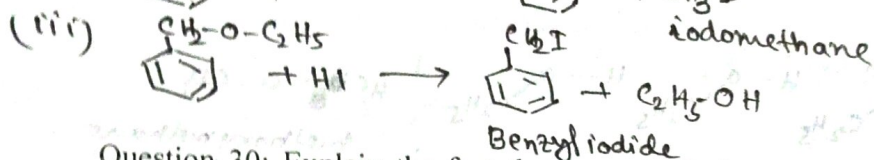
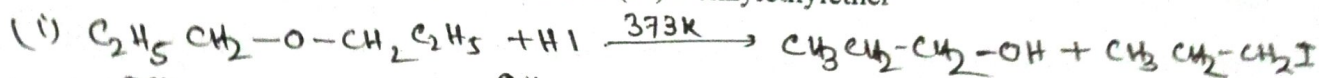
Solution 28: 1-propoxypropane can be synthesized from propan-1-ol by dehydration. Propan-1-ol undergoes dehydration in the presence of protic acids (such as  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ , ...) to give 1-propoxypropane.



Propan-1-ol 1-propoxypropane The mechanism of this reaction involves the following three steps:



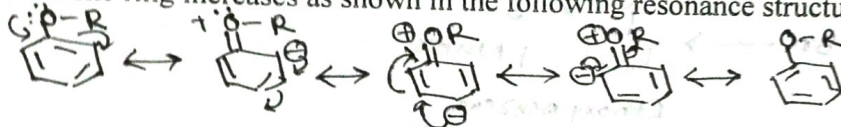
Question 29: Write the equation of the reaction of hydrogen iodide with: (i) 1-propoxypropane (ii) Methoxybenzene and (iii) Benzylethylether



Question 30: Explain the fact that in aryl alkyl ethers. (i) The alkoxy group activates the benzene ring towards electrophilic substitution and (ii) It directs the incoming substituents to ortho and para positions in benzene ring.

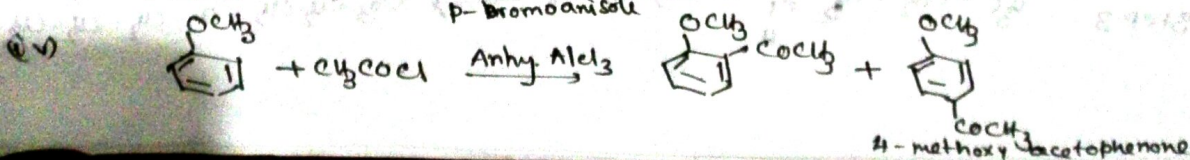
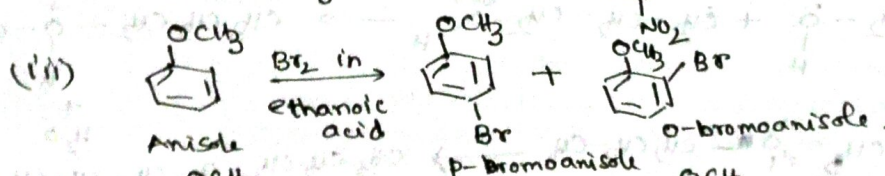
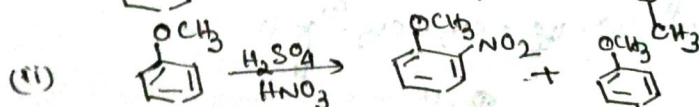
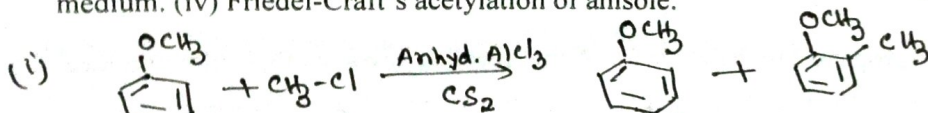
Solution 30:

In aryl alkyl ethers, due to the +R effect of the alkoxy group, the electron density in the benzene ring increases as shown in the following resonance structure.

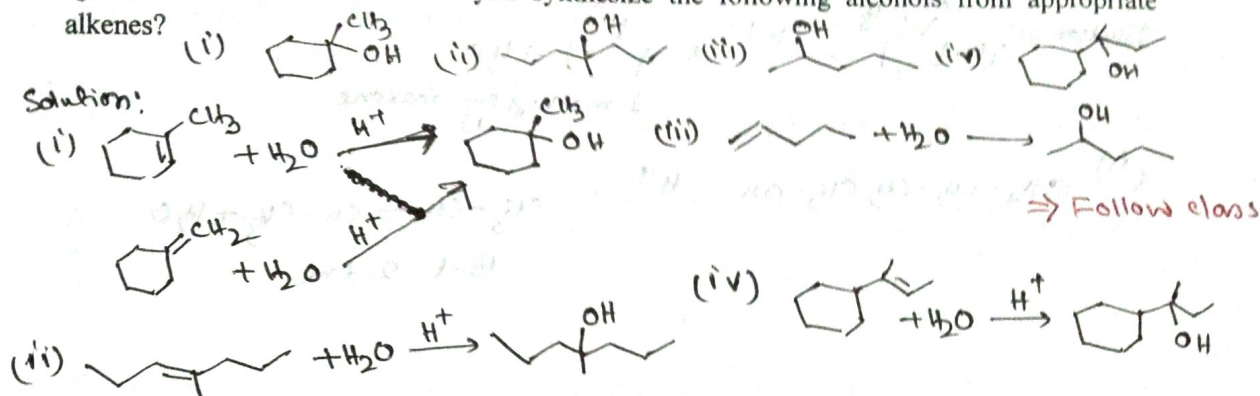


Thus, benzene is activated towards electrophilic substitution by the alkoxy group. (ii) It can also be observed from the resonance structures that the electron density increases more at the ortho and para positions than at the meta position. As a result, the incoming substituents are directed to the ortho and para positions in the benzene ring.

Question 31: Write equations of the following reactions: (i) Friedel-Crafts reaction — alkylation of anisole. (ii) Nitration of anisole. (iii) Bromination of anisole in ethanoic acid medium. (iv) Friedel-Craft's acetylation of anisole.

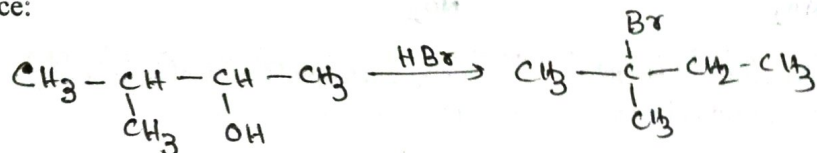


Question 32: Show how would you synthesize the following alcohols from appropriate alkenes?

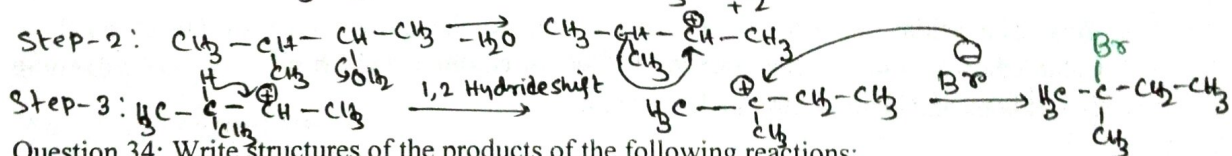
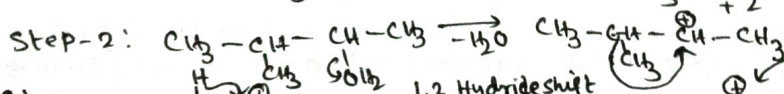
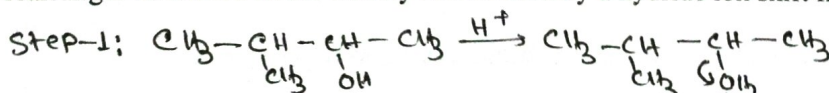


Note: ~~Solution 32~~: The given alcohols can be synthesized by applying Markovnikov's rule of acid-catalysed hydration of appropriate alkenes.

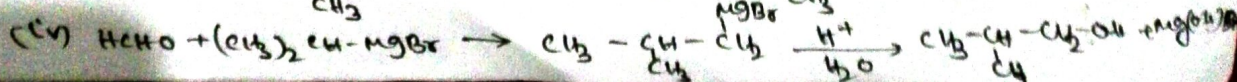
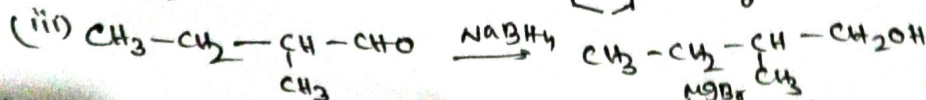
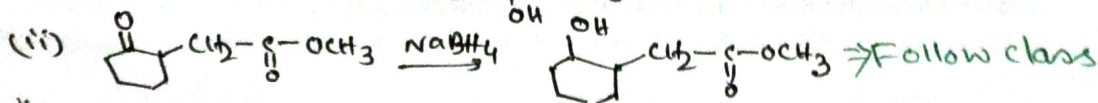
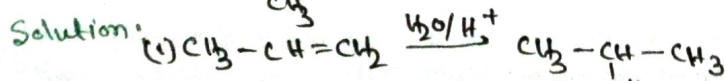
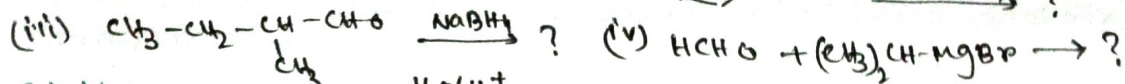
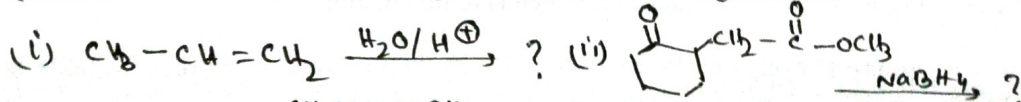
Question 33: When 3-methylbutan-2-ol is treated with HBr, the following reaction takes place:



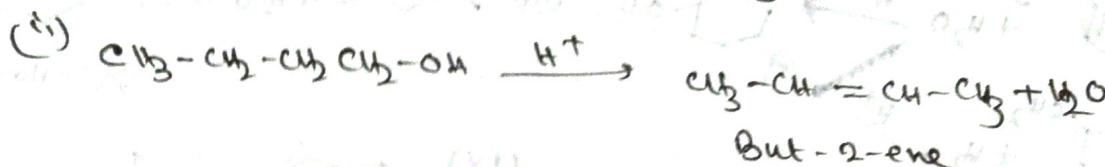
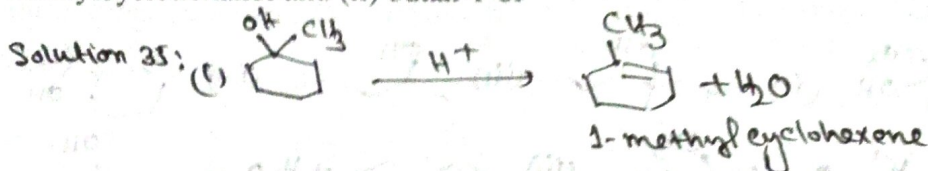
Give a mechanism for this reaction. (Hint: The secondary carbocation formed in step II rearranges to a more stable tertiary carbocation by a hydride ion shift from 3rd carbon atom.)



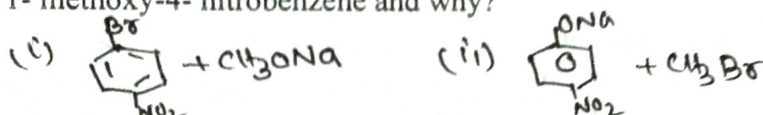
Question 34: Write structures of the products of the following reactions:



Question 35: Predict the major product of acid catalyzed dehydration of (i) 1-methylcyclohexanol and (ii) butan-1-ol



Question 36: Which of the following is an appropriate set of reactants for the preparation of 1-methoxy-4-nitrobenzene and why?



Solution 36: Set (ii) is an appropriate set of reactants for the preparation of 1-methoxy-4-nitrobenzene.



In set (i), sodium methoxide (CH<sub>3</sub>ONa) is a strong nucleophile as well as a strong base. Hence, an elimination reaction predominates over a substitution reaction.

37. Out of 2-chloroethanol and ethanol which is more acidic and why?

Ans. The acidic character of alcohols is due to the polar nature of O—H bond. 2-Chloroethanol, is more acidic due to -I effect of chlorine atom. It increases the polarity of O—H bond and increases the acidic strength.

37. Out of o-nitrophenol and p-nitrophenol, which is more volatile?

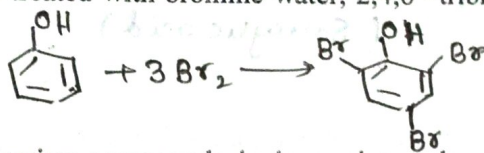
Explain. Ans. o-nitrophenol, due to intramolecular hydrogen bonding, is more volatile in nature. In para-nitrophenol, there is intermolecular hydrogen bonding.

38. Out of o-nitrophenol and o-cresol which is more acidic?

Ans. In substituted phenols, the presence of electron withdrawing groups such as nitro group, enhances the acidic strength of phenol. This effect is more pronounced when such a group is present at ortho and para positions. It is due to the effective delocalisation of negative charge in phenoxide ion. On the other hand, electron releasing groups, such as alkyl groups, in general, do not favour the formation of phenoxide ion resulting in decrease in acid strength. Cresols, for example, are less acidic.

39. When phenol is treated with bromine water, white precipitate is obtained. Give the structure and the name of the compound formed.

Ans. When phenol is treated with bromine water, 2,4,6-tribromophenol is formed as white precipitate.

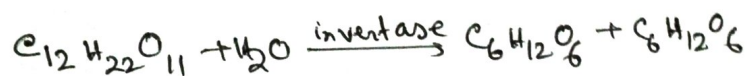


40. Arrange the following compounds in increasing order of acidity and give a suitable explanation. Phenol, o-nitrophenol, o-cresol.

Ans. Increasing order of acidity will be o-cresol < phenol < o-nitrophenol. Explanation: In substituted phenols, the presence of electron withdrawing groups such as nitro group, enhances the acidic strength of phenol. This effect is more pronounced when such a group is present at ortho and para positions. It is due to the effective delocalization of negative charge in phenoxide ion. On the other hand, electron releasing groups, such as alkyl groups, in general, do not favour the formation of phenoxide ion resulting in decrease in acid strength. Cresols, for example, are less acidic.

41. Name the enzymes and write the reactions involved in the preparation of ethanol from sucrose by fermentation.

Ans. Ethanol,  $C_2H_5OH$ , is obtained commercially by fermentation, the oldest method is from sugars. The sugar in molasses, sugarcane or fruits such as grapes is converted to glucose and fructose, (both of which have the formula  $C_6H_{12}O_6$ ), in the presence of an enzyme, invertase.



42. How can propan-2-one be converted into tert-butyl alcohol?

Ans. Using Grignard reagent.

*Mechanism Follow class*

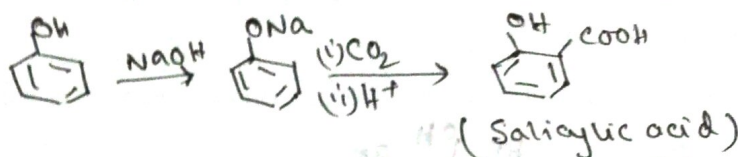
43. Why is the reactivity of all the three classes of alcohols with conc. HCl and  $ZnCl_2$  (Lucas reagent) different?

Ans. Reaction with hydrogen halides: Alcohols react with hydrogen halides to form alkyl halides.  $ROH + HX \rightarrow R-X + H_2O$ , The difference in reactivity of three classes of alcohols with HCl distinguishes them from one another (Lucas test). Alcohols are soluble in Lucas reagent

(conc. HCl and ZnCl<sub>2</sub>) while their halides are immiscible and produce turbidity in solution. In case of tertiary alcohols, turbidity is produced immediately as they form the halides easily. Primary alcohols do not produce turbidity at room temperature. The reaction is followed by the formation of carbocation since tertiary carbocation is most stable.

The order of reactivity will be  $3^\circ > 2^\circ > 1^\circ$ .

44. Write steps to carry out the conversion of phenol to aspirin.



45. Explain why low molecular mass alcohols are soluble in water.

Ans. The low molecular mass alcohols are soluble in water due to the presence of intermolecular hydrogen bonding between their molecules. Polar O-H group favours dissolution process whereas non polar alkyl group does not. As the size of the alkyl group increases, it overcomes the effect of the polar nature -OH group and the solubility decreases.

46. Explain why p-nitrophenol is more acidic than phenol.

Ans. In substituted phenols, the presence of electron withdrawing groups such as nitro groups, enhances the acidic strength of phenol. This effect is more pronounced when such a group is present at ortho and para positions. It is due to the effective delocalisation of negative charge in phenoxide ion.

47. Explain why alcohols and ethers of comparable molecular mass have different boiling points? Ans. The high boiling points of alcohols are mainly due to the presence of intermolecular hydrogen bonding in them which is lacking in ethers

48. o-Nitrophenol is less soluble in water than the m- and p-isomers.

Explanation: Due to intramolecular hydrogen bonding o-Nitrophenol does not form hydrogen bond with water.

(c) Explain why Lewis acid is not required in bromination of phenol?

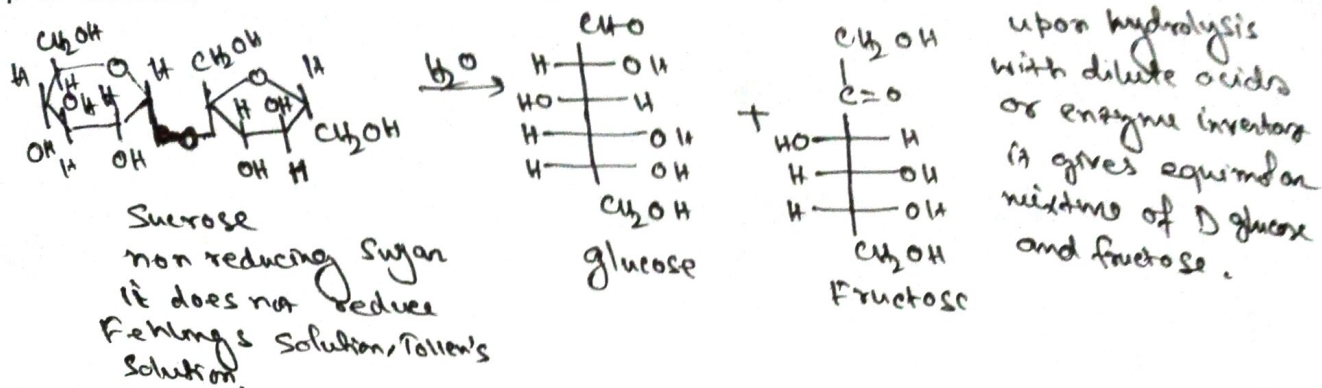
Ans. The usual halogenations of benzene takes place in the presence of a Lewis acid, such as FeBr<sub>3</sub>, which polarises the halogen molecule. In case of phenol, the polarisation of bromine molecule takes place even in the absence of Lewis acid. It is due to the highly activating effect of -OH group attached to the benzene ring.

⇒ Follow class

**Question 49:**

What are the hydrolysis products of (i) sucrose and ~~fructose~~?

**Solution 49:(i)** On hydrolysis, sucrose gives one molecule of  $\alpha$ -D-glucose and one molecule of  $\beta$ -D-fructose.

**Question 50:**

What do you understand by the term glycosidic linkage?

**Solution 50:**

Glycosidic linkage refers to the linkage formed between two monosaccharide units through an oxygen atom by the loss of a water molecule. For example, in a sucrose molecule, two monosaccharide units,  $\alpha$ -glucose and  $\beta$ -fructose, are joined together by a glycosidic linkage.

**51. (a) Arrange the following compounds in the increasing order of their acid strength :**

p-cresol, p-nitrophenol, phenol

(b) Write the mechanism (using curved arrow notation) of the following reaction:

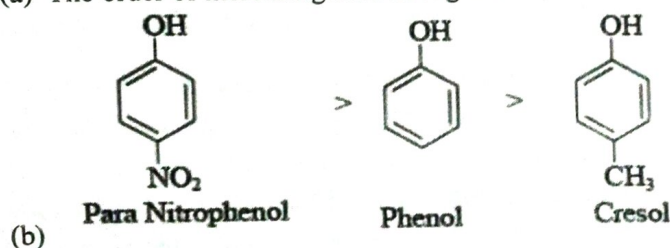
Write the structures of the products when Butan-2-ol reacts with the following:

(a)  $\text{CrO}_3$

(b)  $\text{SOCl}_2$

**Solution:**

(a) The order of increasing acid strength is

**Reason: -**

Since the  $-\text{NO}_2$  group is (-M) group so it withdraw the  $e^-$  density from benzene. A stabilized the conjugate Base of para nitrophenol so "higher the stability of conjugate base more will be the reactivity of corresponding acids" while in case of cresol +H effect of Methyl group destabilised conjugate base.

(c) Mechanism: -

